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⑤④ Phosphate coating metal surfaces.

⑤⑦ Metal surfaces are phosphated by acidic aqueous phosphate solutions containing:

- (a) from 0.1 to 2 g/l of zinc ion;
- (b) from 5 to 50 g/l of phosphate ion;
- (c) from 0.2 to 4 g/l of manganese ion;
- (d) at least 0.05 g/l of fluoride ion; and
- (e) a phosphating accelerator.

The phosphated metal surface is suitable for electrocoating.

PHOSPHATE COATING METAL SURFACES

The present invention relates to an acidic aqueous phosphate solution and a process for phosphating a metal surface with the solution. More particularly, it relates to a solution and a process for forming a phosphate film especially suitable for cationic electrocoating, and is particularly applicable to metal which includes an iron-based surface and a zinc-based surface such as an automobile body.

Japanese Patent Publication (unexamined) No. 107784/1980 (laid-open to the public on August 19, 1980) discloses a process for treating a metal surface by dip treatment, followed by spray treatment, with an acidic aqueous phosphate solution containing from 0.5 to 1.5 g/l of zinc ion, from 5 to 30 g/l of phosphate ion, and from 0.01 to 0.2 g/l of nitrite ion and/or from 0.05 to 2 g/l of m-nitrobenzene-sulphonate ion. The process is reported to be capable of providing a phosphate film which is effective for forming a coating by cationic electrocoating having excellent adhesion and corrosion-resistance on complicated articles having many pocket portions like car bodies.

Japanese Patent Publication (unexamined) No. 145180/1980 (laid-open to the public on November 12, 1980) discloses a process for treating a metal surface by spray treatment with an acidic aqueous phosphate solution containing from 0.4 to 1.0 g/l of zinc ion, from 5 to 40 g/l of phosphate ion, from 2.0 to 5.0 g/l of chlorate ion, and from 0.01 to 0.2 g/l of nitrite ion. Further, Japanese Patent Publication (unexamined)

No. 152183/1980 (laid open to the public on November 27, 1980) discloses an acidic aqueous phosphate solution containing from 0.08 to 0.20 weight % of zinc ion, from 0.8 to 3.0 weight % of phosphate ion, from 0.05 to 0.35 weight % of chlorate ion, from 0.001 to 0.10 weight % of nitrite ion, and complex fluoride ion in an amount calculated by the formula : $0.4 \geq y \geq 0.63x - 0.042$, wherein x is the concentration in weight % of zinc ion and y is the concentration in weight % of the complex fluoride ion. These prior art processes are reported to be capable of providing excellent adhesion and corrosion-resistance to the coating by cationic electrocoating.

However, in a recent development in the automobile industry there has come to be used for car bodies steel components plated on one surface only with zinc or alloyed zinc, with the object of further improving corrosion-resistance after the application of the siccative coating. It has come to be recognized, however, that when the above-mentioned prior art compositions and processes are applied to such materials (i.e. to metal which includes both an iron-based surface and a zinc-based surface), on the iron-based surface a phosphate film suitable as a substrate to be coated by cationic electrocoating can be formed as desired, but a phosphate film formed on the zinc-based surface is significantly inferior to that formed on the iron-based surface.

There has been developed a composition and process to solve the above-mentioned problems which occur on zinc-based surfaces in components which include both an iron-based surface and a zinc-based surface. This composition and process are disclosed in Japanese Patent Publication (unexamined) No. 152472/1982 (laid-open to

the public on September 20, 1982). That Publication discloses dipping the metal surface in an acidic aqueous phosphate solution comprising from 0.5 to 1.5 g/l of zinc ion, from 5 to 30 g/l of phosphate ion, from 0.6 to 5 3 g/l of manganese ion, and a phosphating accelerator.

The present invention represents an improvement in the above-mentioned techniques for phosphating, particularly as a substrate treatment under cationic electrocoating.

10 The present invention provides an acidic aqueous phosphate solution and process which can give a phosphate film capable of providing excellent adhesion and corrosion-resistance to coatings particularly from cationic electrocoating. The solution and
15 process provide excellent phosphate films on metal which includes both an iron-based surface and a zinc-based surface. Furthermore, the solution and process can give the phosphate film by treatment at low temperature. Moreover, the phosphate film can be satisfactorily formed on an article having a complicated shape like a
20 car body.

Accordingly, the invention provides an acidic aqueous phosphate solution for phosphating a metal surface, the solution containing:

- 25 a) from about 0.1 to about 2 g/l, preferably from about 0.5 to about 1.5 g/l, of zinc ion;
- b) from about 5 to about 50 g/l, preferably from about 10 to about 30 g/l, of phosphate ion;
- 30 c) from about 0.2 to about 4 g/l, preferably from about 0.6 to about 3 g/l, of manganese ion;
- d) at least about 0.05 g/l, preferably from about 0.1 to about 3 g/l, of a fluoride ion; and

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e) a phosphating accelerator (conversion coating accelerator) which is preferably one or more of the following:

- 5 i) from about 0.05 to about 3 g/l, preferably from about 0.05 to about 1.9 g/l, and more preferably from about 0.2 to about 1.5 g/l, of chlorate ion;
- ii) from about 0.01 to about 0.2 g/l, preferably from about 0.04 to about 0.15 g/l,
10 of nitrite ion;
- iii) from about 1 to about 10 g/l, preferably from about 2 to about 8 g/l, of nitrate ion;
- (iv) from about 0.5 to about 5 g/l, preferably from about 1 to about 1.5 g/l, of hydrogen
15 peroxide (based on 100% H_2O_2);
- v) from about 0.05 to about 2 g/l, preferably from about 0.1 to about 1.5 g/l, of m-nitrobenzene-sulphonate ion;
- vi) from about 0.05 to about 2 g/l, preferably
20 from about 0.1 to about 1.5 g/l, of m-nitrobenzoate ion; and
- vii) from about 0.05 to about 2 g/l, preferably from about 0.1 to about 1.5 g/l, of p-nitrophenol.

The invention also provides a process for phosphating
25 a metal surface, which process comprises treating the surface with this solution.

The invention provides also an aqueous concentrated composition for use in formulating an acidic aqueous phosphate solution, the concentrated composition comprising
30 zinc ion, phosphate ion, manganese ion and fluoride ion in a weight proportion of 0.1 to 2 : 5 to 50 : 0.2 to 4 : not less than 0.05 respectively.

The metal surfaces treated in accordance with the present invention include iron-based surfaces, zinc-based surfaces, aluminium-based surfaces, and their respective alloy-based surfaces. These metal surfaces
5 can be treated either separately or in combination. The advantage of the present invention is most prominently exhibited when the treatment is carried out on metal which includes both an iron-based surface and a zinc-based surface, as, for example, in a car body. Examples
10 of zinc-based surfaces include galvanized steel plate, galvanealed steel plate, electrogalvanized steel plate, electro zinc-alloy plated steel plate and complex electrogalvanized steel plate.

When the content of the zinc ion in the present
15 acidic phosphate solution is less than about 0.1 g/l, an even phosphate film is not formed on iron-based surfaces. When the zinc ion content exceeds about 2 g/l, on both iron-based and zinc-based surfaces continuing formation of the phosphate film occurs,
20 causing a build up of the film, with the result that the film shows a decrease in adhesion and becomes unsuitable as a substrate for cationic electrocoating.

When the content of phosphate ion in the solution is less than about 5 g/l, an uneven phosphate film tends to be formed. When the phosphate ion content is more
25 than 50 g/l, no further benefit results, and it is therefore economically disadvantageous to use greater quantities of phosphate chemicals.

When the content of manganese ion is less than 0.2 g/l, the manganese content in the phosphate film formed on zinc-based surfaces is so small that the adhesion
30 between the substrate and the coating after cationic electrocoating becomes insufficient. When the manganese ion is present in an amount of more than 4 g/l, no further beneficial effects are obtained for the coating, and the solution forms excessive precipitates, making it
35 impossible to obtain a stable solution.

The manganese content in the phosphate film formed on the metal substrates should be in the range of from about 1 to about 20 % by weight, based on the weight of the film, in order to have a phosphate film which exhibits the performance requirements for cationic electrocoating. The phosphate film containing this amount of manganese also forms part of the present invention.

The content of manganese in the phosphate film can be determined according to conventional procedures. For example, a phosphated test piece [$S(m^2)$; $W_1(g)$; where S represents its surface area and W_1 its weight] is dipped in an aqueous solution of 5% by weight chromic acid at $75^\circ C$ for 5 minutes to dissolve the film, and the weight of the test piece after treatment [$W_2(g)$] is measured. The amount of film [$W_C(g/m^2)$] is found from the formula: $[W_C = (W_1 - W_2)/S]$. Then, the amount of manganese which dissolved into the aqueous solution of chromic acid [$A(l)$, where A represents the volume of the solution] is determined by the atomic light absorption process [$M(g/l)$] to obtain the total amount of the dissolved manganese [$W_M - A.M/S (g/m^2)$]. Using the thus obtained amount and the thus obtained film amount, the manganese content can be calculated from the formula $(W_M/W_C) \times 100\%$

When the amount of fluoride ion in the phosphating solution is less than 0.05 g/l, micronization of the phosphate film, improvement of corrosion-resistance after coating, and phosphating treatment at a reduced temperature cannot be attained. the fluoride ion can be present in an amount above 3 g/l, but use in such quantities does not provide any greater effects than are obtainable by smaller amounts. Preferably, the fluoride ion is in the form of a complex fluoride ion, e.g. the fluoroborate ion or the fluorosilicate ion, although the F^- ion itself can also be used. However the fluoride ion is provided, it is measured in terms of F ions.

When phosphating accelerator is present in less than the amounts specified above, a sufficient quantity of phosphate film is not formed on iron-based surfaces, giving rise to yellow rust and other defects. On the other hand, when the accelerator content is greater than the amounts specified above, a blue coloured uneven film often forms on an iron-based surface. However, when the solution contains from >1 g/l to about 2 g/l of zinc ion, it is possible to obtain a satisfactory phosphate film when chlorate is used as the accelerator in an amount in excess of 2 g/l, e.g. from 2 g/l to 5 g/l. However, the use of such high levels of chlorate is not preferred.

In the present phosphating solutions, it is preferable that the weight ratio of zinc ion to phosphate ion be 1 : (10 to 30). In this range, an even phosphate film is obtained which exhibits all the performance requirements needed for cationic electrocoating. The weight ratio of zinc ion to manganese ion is preferably 1 : (0.5 to 2). In this range, it is possible to obtain in an economic manner a phosphate film which contains the required amount of manganese and which displays all the beneficial effects.

It is desirable for the present phosphating solutions to have a total acidity of 10 to 50 points, a free acidity of 0.3 to 2.0 points, and an acid ratio of 10 to 50. With the total acidity in this range, the phosphate film can be obtained economically, and with the free acidity in this range, the phosphate film can be obtained evenly without excessive etching of the metal surface. Adjustments in the solution to obtain and maintain these points and this ratio can be achieved by use of an alkali metal hydroxide or ammonium hydroxide as required.

Sources of the ingredients of the present phosphating solutions include the following: as to the zinc ion, zinc oxide, zinc carbonate, zinc nitrate, etc.; as to the phosphate ion, phosphoric acid, zinc phosphate, zinc monohydrogen phosphate, zinc dihydrogen phosphate, manganese phosphate, manganese monohydrogen phosphate, manganese dihydrogen phosphate, etc.; as to the manganese ion, manganese carbonate, manganese nitrate, manganese chloride, the above-mentioned manganese phosphate compounds, etc.; as to the fluoride ion, hydrofluoric acid, fluoroboric acid, fluorosilicic acid, fluorotitanic acid, and their metal salts (e.g. zinc salt, nickel salt; however, the sodium salt is excluded as it does not produce the desired effect); and as to the phosphating accelerator, sodium nitrite, ammonium nitrite, sodium m-nitrobenzene-sulphonate, sodium m-nitrobenzoate, aqueous hydrogen peroxide, sodium chlorate, ammonium chlorate, nitric acid, sodium nitrate, zinc nitrate, manganese nitrate, nickel nitrate, etc.

The present phosphating solutions can further contain, as an optional ingredient, nickel ion. The content of the nickel ion should be from about 0.1 to about 4 g/l, preferably about 0.3 to about 2 g/l. When nickel ion is present with manganese ion, performance of the resulting phosphate film is further improved, i.e. the adhesion and corrosion-resistance of the coating obtained after cationic electrocoating are further improved. In phosphating solutions containing nickel ion, the weight ratio of zinc ion to the sum of manganese ion and the nickel ion is desirably 1 : (0.5 to 5.0), preferably 1 : (0.8 to 2.5). The supply source of nickel ion can be, for example, nickel carbonate, nickel nitrate, nickel chloride, nickel phosphate, etc.

The phosphate film formed by the present solutions is a zinc phosphate-type film. Such films formed on iron-based metal surfaces usually contain from about 25 to about 40 weight % of zinc, from about 3 to about 11 weight % of iron, from about 1 to about 20 weight % of manganese, and from 0 to about 4 weight % of nickel. Such films formed on zinc-based metal surfaces usually contain from about 30 to about 45 weight % of zinc, from about 1 to about 20 weight % of manganese, and from 0 to about 4 weight % of nickel.

The process of the invention for phosphating metal surfaces by use of the present phosphating solutions can be carried out by spray treatment, dip treatment, or by a combination of such treatments. Spray treatment can usually be effected by spraying for 5 or more seconds in order to form an adequate phosphate film which exhibits the desired performance characteristics. This spray treatment can be carried out using a cycle comprising first a spray treatment for about 5 to about 30 seconds, followed by discontinuing the treatment for about 5 to about 30 seconds, and then spray treating again for at least 5 seconds, with a total spray treatment time of at least 40 seconds. This cycle can be carried out once, twice or three times.

Dip treatment is an embodiment which is preferred to spray treatment in the process of the invention. In order to form an adequate phosphate film which exhibits the desired performance characteristics, the dip treatment is usually effected for at least 15 seconds, preferably for about 30 to about 120 seconds. Also, a treatment using a combination of spray treatment and dip treatment can be carried out by first dip treating for at least 15 seconds and then spray treating for at least 2 seconds. Alternatively, the treatment can be effected by first spray treating for at least 5 seconds, and then

dip treating for at least 15 seconds. The combination of first dip treating and then spray treating is especially advantageous for articles having complicated shapes like a car body. For such articles, it is preferable to first carry out a dip treatment for from about 30 to about 90 seconds, and then carry out the spray treatment for from about 5 to about 45 seconds. In this process, it is advantageous to effect the spray treatment for as long a time as is possible within the limitations of the automotive production line, in order to remove the sludge which adheres to the article during the dip treatment stage.

In the present process, the treating temperature can be from about 30 to about 70°C, for example between 30 and 40°C though preferably from about 35 to about 60°C. These lower limits are approximately 10 to 15°C lower than those of the prior art processes. Treating temperatures below 30°C should not be used due to the increased time required to produce an acceptable coating. When the treating temperature is too high, the phosphating accelerator is decomposed and excess precipitate is formed causing the components in the solution to become unbalanced and making it difficult to obtain satisfactory phosphate films.

In spray treatments, a convenient spray pressure is from 0.6 to 2 Kg/cm² G.

As described above, a preferred mode of treatment in the process of the present invention is a dip treatment or a combined treatment using a dip treatment first and then a spray treatment.

An advantageous procedure for treating metal surfaces using a series of pre-coating treatment steps followed by phosphating in accordance with the process of the present invention is as follows:

A metal surface is first subjected to a spray treatment and/or a dip treatment with an alkaline degreasing agent at a temperature of 50 to 60°C for 2 minutes; followed by washing with tap water; spray treatment and/or dip treatment with a surface conditioner at room temperature for 10 to 30 seconds; dip treatment with the solution of the present invention at a temperature of about 30 to about 70°C for at least 15 seconds; and washing with tap water and then with deionized water, in that order. Thereafter, it is desirable to after-treat with an acidulated rinse common to the industry such as a dilute chromate solution. This after-treatment is preferably adopted even when the process of the present invention is carried out by spray treatment, or by a combined treatment comprising a spray treatment followed by a dip treatment. By introducing this after-treatment, a phosphate film which gives greater corrosion-resistance to a siccative coating can be obtained.

When carrying out the dip treatment or the dip treatment followed by spray treatment, which is the preferred treating method of the present invention, it is advantageous to use an acidic aqueous phosphate solution comprising:

- a') from about 0.5 to about 1.5 g/l, preferably from about 0.7 to about 1.2 g/l, of zinc ion,
- b') from about 5 to about 30 g/l, preferably from about 10 to about 20 g/l, of phosphate ion,
- c') from about 0.6 to about 3 g/l, preferably from about 0.8 to about 2 g/l, of manganese ion,
- d') at least about 0.05 g/l, preferably from about 0.1 to about 2 g/l, of a fluoride ion, and
- e') a phosphating accelerator, preferably that and its quantity given above.

(hereinafter referred to as the "dipping solution").

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When using this dipping solution especially on a metal which includes both an iron-based surface and a zinc-based surface, there is formed thereon in an economical manner a fine, even, and dense phosphate film which provides excellent adhesion and corrosion resistance to coatings formed by cationic electrocoating.

The present invention further provides a concentrated aqueous composition for formulating the acidic aqueous phosphate solutions of the present invention. The acidic aqueous treating solutions are conveniently prepared by diluting an aqueous concentrate which contains a number of the solution ingredients in proper weight ratios, and then adding other ingredients as needed to prepare the treating solutions of the invention. The concentrates are advantageously formulated to contain zinc ion, phosphate ion, manganese ion, fluoride ion, and optionally, nickel ion, in a weight proportion of 0.1 to 2 : 5 to 50 : 0.2 to 4 : at least 0.05 : 0.1 to 4. The concentrates preferably contain a weight proportion of the above ingredients of 0.5 to 1.5 : 10 to 30 : 0.6 to 3 : 0.1 to 3 : 0.3 to 2 ; the nickel ion proportion is only relevant, of course, when nickel ion is present. The concentrates are preferably formulated to contain at least about 25 g/l, more preferably from about 50 g/l to about 130 g/l, of zinc ion. However, care should be taken in forming the concentrates. For example, when manganese ion and complex fluoride ion are present together in a concentrate with sodium ion and/or chlorate ion, a precipitate is formed. Also, it is not advisable to add any phosphating accelerator to the concentrate, since the accelerators tend to decompose and cause other problems.

As an example of a useful concentrated aqueous composition, there is formulated a concentrated composition comprising 3.0 weight % of zinc oxide, 1.8 weight % of nickel carbonate (II), 48.2 weight % of 75 %
5 phosphoric acid, 10.0 weight % of manganese nitrate (II) hydrate (20 weight % manganese content), 7.9 weight % of 40 % fluorosilicic acid, and 29.1 weight % of water. This concentrate can then be diluted with water to 2.5 volume %, followed by the addition of an aqueous
10 solution of 20 % sodium nitrite to give an acidic phosphating solution of the invention.

The metal surface which has been phosphated is preferably rinsed and electrocoated, preferably cationic electrocoated.

15 The invention is illustrated by the following Examples and comparative Examples, the Examples illustrating preferred embodiments of the invention.

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Examples 1 to 8 and Comparative Examples 1 to 8

(1) Metal to be subjected to treatment:

Galvanealed steel plate

Electrogalvanized steel plate

5 Electro zinc-alloy plated steel plate

Cold rolled steel plate.

(2) Acidic aqueous phosphate solution:

Those having the compositions shown in Table 1 were used.

(3) Treating process:

10 The surfaces of the above-mentioned 4 kinds of metal were simultaneously treated by the following steps:

Degreasing→water washing→surface conditioning→
phosphating→water washing→pure water washing→drying→
coating.

15 (4) Treating conditions:

(a) Degreasing:

Using an alkaline degreasing agent ("RIDOLINE SD200" made by Nippon Paint Co., 2 weight % concentration), spray treatment was carried out at 60°C for 1 minute,
20 followed by dip treatment for 2 minutes.

(b) Washing with water:

Using tap water, washing was carried out at room temperature for 15 seconds.

(c) Surface conditioning:

25 Using a surface conditioning agent ("FIXODINE 5N-5" made by Nippon Paint Co., 0.1 weight % concentration), dip treatment was carried out at room temperature for 15 seconds.

(d) Phosphating:

30 Using the above-mentioned aqueous phosphate solution, dip treatment was carried out at 52°C for 120 seconds, except that in Example 5, dip treatments were carried out at 52°C and 40°C.

(e) Water washing:

35 Using tap water, washing was carried out at room temperature for 15 seconds.

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(f) Pure water washing:

Using deionized water, dip treatment was carried out at room temperature for 15 seconds.

(g) Drying was carried out with hot blown air at 100°C for 10 minutes.

The appearance of each phosphated plate thus obtained and the weight of its phosphate film were determined.

(h) Coating:

10 A cationic electrocoating composition ("POWER TOP U-30 Dark Grey" made by Nippon Paint Co.) was coated to a film thickness of 20 μ (voltage 180 V, electricity applying time 3 minutes), and the surface was baked at 180°C for 30 minutes. Some of the resulting electrocoated 15 plates were used for the brine spray test.

The remaining electrocoated plates were coated with an intermediate coating composition ("ORGA TO778 Grey" made by Nippon Paint Co.) to a film thickness of 30 μ , then with a top coating composition ("ORGA TO626 Margaret 20 White" made by Nippon Paint Co.) to a film thickness of 40 μ to obtain coated plates having a total of 3 coatings and 3 bakings, and these plates were then used for the adhesion test and the spot rust test.

(5) Test results:

25 The results are shown in Table 2. Each test method is described below.

(a) Brine spray test (JIS-Z-2871):

Cross-cuts were made on the electrocoated plate, and 5% brine was then sprayed on the plate for 30 500 hours (zinc-plated steel plate) or 1,000 hours (cold rolled steel plate).

(b) Adhesion test:

The coated plate was dipped in deionized water at 50°C for 10 days, after which it was provided with 35 grids (100 squares each) made at 1 mm intervals or at 2 mm intervals using a sharp cutter. To each surface

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of the thus treated plate, an adhesive tape was applied after which it was peeled off and the number of the remaining coated squares on the coated plate was counted.

(c) Spot rust test:

5 The coated plate was supported in an inclined position at an angle of 15° to the horizontal plane. An arrow having a weight of 1.00 g, a total length of 14.0 mm, and a conical head made of an alloy tool steel (material quality: JIS G-4404, hardness: Hv 700 or
10 higher) was repeatedly allowed to fall perpendicularly by its own weight from a height of 150 cm onto the inclined plate, until damage to the coating surface had occurred at 25 places thereon. Thereafter, the coated plate was subjected to 4 test cycles, each cycle consisting of a
15 brine spray test (JIS-Z-2871, 24 hours)→ a humidity test (temperature 40°C ; relative humidity 85%, 120 hours)→ followed by standing in a room (for 24 hours). After the test, the average values (mm) of the maximum diameter of spot rusts and blisters on the coated surfaces were
20 determined.

Additionally, scanning electron microscope photographs of the crystals of some of the phosphate films were taken and these are reproduced as follows in the accompanying drawings:

25	Galvanealed <u>steel plate</u>	Cold rolled <u>steel plate</u>
Example 1	Figure 1	Figure 2
Comparative Example 1	Figure 3	Figure 4

Table 1

Composition of acidic aqueous phosphate solution	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Zn ion (g/l)	1.0	1.0	1.0	1.0	1.0	1.0	0.7	1.2
PO ₄ ion (")	14.0	14.0	14.0	14.0	14.0	14.0	10.0	20.0
Mn ion (")	0.8	2.0	0.8	2.0	0.8	0.8	0.8	0.8
Ni ion (")	-	-	0.3	0.3	0.3	0.3	0.3	0.3
SiF ₆ ion (") (as F ion)	1.0	1.0	1.0	1.0	2.0*	1.0	1.0	1.0
NO ₂ ion (")	0.06	0.06	0.06	0.06	0.06	-	0.06	0.06
H ₂ O ₂ (")	-	-	-	-	-	1.0	-	-
NO ₃ ion (")	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
ClO ₃ ion (")	0.7	0.7	0.7	0.7	-	0.7	0.7	0.7
Total acidity (Point)	18.5	20.0	19.5	20.5	20.0	19	14	25
Free acidity (")	0.9	0.9	0.9	0.9	0.9	0.9	0.7	1.0
Acid ratio	21	22	22	23	22	21	20	25

Remarks) *: combination of SiF₆ ion and BF₄ ion in a weight proportion of 1:1 (each as F ion)

Table 1 (continued)

Composition of acidic aqueous phosphate solution	Com. Example 1	Com. Example 2	Com. Example 3	Com. Example 4	Com. Example 5	Com. Example 6	Com. Example 7	Com. Example 8
Zn ion (g/l)	1.0	1.0	1.0	1.0	1.0	1.0	0.7	1.2
PO ₄ ion (g/l)	14.0	14.0	14.0	14.0	14.0	14.0	10.0	20.0
Mn ion (g/l)	0.8	2.0	-	0.8	2.0	0.8	0.8	0.8
Ni ion (g/l)	-	-	0.3	0.3	0.3	0.3	0.3	0.3
SiF ₆ ion (g/l)	-	-	1.0	-	-	-	-	-
(as F ion)	-	-	1.0	-	-	-	-	-
NO ₂ ion (g/l)	0.06	0.06	0.06	0.06	0.06	-	0.06	0.06
H ₂ O ₂ (g/l)	-	-	-	-	-	1.0	-	-
NO ₃ ion (g/l)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
ClO ₃ ion (g/l)	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Total acidity (Point)	17.5	19	18.5	18	19.5	18	13	24
Free acidity (Point)	0.9	0.9	0.9	0.9	0.9	0.9	0.7	1.0
Acid ratio	19	21	21	20	22	20	19	24

Table 2

Metal	Test items	Example 1	Example 2	Example 3	Example 4	Example 5 (treatment at 52°C)	Example 5 (treatment at 40°C)
Galva- nealed steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m ²)	2.8	2.6	2.7	2.5	2.3	2.2
	Brine spray- ing (mm)	2.0	1.5	1.0	1.0	1.0	1.0
Electro- galva- nized steel plate	Adhesion	100/100	100/100	100/100	100/100	100/100	100/100
	2mm	100/100	100/100	100/100	100/100	100/100	100/100
	1mm	100/100	100/100	100/100	100/100	100/100	100/100
Electro- zinc- alloy plated steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m ²)	2.3	2.1	2.2	2.1	2.0	1.9
	Brine spray- ing (mm)	3.0	2.0	1.5	1.5	1.0	1.0
Electro- zinc- alloy plated steel plate	Adhesion	100/100	100/100	100/100	100/100	100/100	100/100
	2mm	100/100	100/100	100/100	100/100	100/100	100/100
	1mm	100/100	100/100	100/100	100/100	100/100	100/100

19(a)

Table 2 (continued)

Metal	Test items	Example 1	Example 2	Example 3	Example 4	Example 5 (treatment at 52°C)	Example 5 (treatment at 40°C)
Cold rolled steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.0	1.9	1.9	1.8	1.8	1.8
	Brine spray- ing (mm)	1.0	1.0	1.0	1.0	1.0	1.0
	Adhesion 2mm 1mm	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100
	Spot rust (mm)	0.95	0.95	0.93	0.91	0.90	0.91

Table 2 (continued)

Metal	Test items	Example 6	Example 7	Example 8
Galvanealed steel plate	Film appearance 2 Film weight (g/m ²) Brine spraying (mm) Adhesion 2mm 1mm	Even, dense, excellent 2.8 1.5 100/100 100/100	Even, dense, excellent 2.6 1.0 100/100 100/100	Even, dense, excellent 2.7 1.5 100/100 100/100
Electro-galvanized steel plate	Film appearance 2 Film weight (g/m ²) Brine spraying (mm) Adhesion 2mm 1mm	Even, dense, excellent 2.2 2.5 100/100 100/100	Even, dense, excellent 2.1 2.0 100/100 100/100	Even, dense, excellent 2.1 2.0 100/100 100/100
Electro zinc-alloy plated steel plate	Film appearance 2 Film weight (g/m ²) Brine spraying (mm) Adhesion 2mm 1mm	Even, dense, excellent 2.7 1.5 100/100 100/100	Even, dense, excellent 2.8 1.5 100/100 100/100	Even, dense, excellent 2.7 1.5 100/100 100/100
Cold rolled steel plate	Film appearance 2 Film weight (g/m ²) Brine spraying (mm) Adhesion 2mm 1mm Spot rust (mm)	Even, dense, excellent 2.1 1.0 100/100 100/100 0.97	Even, dense, excellent 2.0 1.0 100/100 100/100 0.95	Even, dense, excellent 2.0 1.0 100/100 100/100 0.96

Table 2 (continued)

Metal	Test items	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Galva-nealed steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	3.2	2.8	4.0	3.0	2.7
	Brine spraying (mm)	2.5	2.0	3.0	1.5	1.5
Electro-galvanized steel plate	Adhesion 2mm	100/100	100/100	65/100	100/100	100/100
	Adhesion 1mm	100/100	100/100	0/100	100/100	100/100
	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
Electro-galvanized steel plate	Film weight (g/m^2)	2.5	2.0	3.2	2.2	2.4
	Brine spraying (mm)	3.5	3.0	6.0	2.5	2.0
	Adhesion 2mm	100/100	100/100	30/100	100/100	100/100
Electro-zinc alloy plated steel plate	Adhesion 1mm	80/100	90/100	0/100	95/100	100/100
	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	3.2	2.9	3.5	3.1	2.8
Electro-zinc alloy plated steel plate	Brine spraying (mm)	2.0	2.0	2.5	2.0	1.5
	Adhesion 2mm	100/100	100/100	72/100	100/100	100/100
	Adhesion 1mm	100/100	100/100	12/100	100/100	100/100

Table 2 (continued)

Metal	Test items	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Cold rolled steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.5	2.2	2.3	2.3	2.0
	Brine spraying (mm)	1.5	1.0	1.0	1.0	1.0
	Adhesion	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100
	Spot rust (mm)	0.96	1.00	0.98	0.98	0.96

20(b)

Table 2 (continued)

Metal	Test items	Comparative Example 6	Comparative Example 7	Comparative Example 8
Galvanealed steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	3.2	2.9	2.7
	Brine spraying (mm)	1.5	1.5	1.5
	Adhesion	100/100	100/100	100/100
Electro-galvanized steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.1	2.3	2.3
	Brine spraying (mm)	3.0	2.5	2.5
	Adhesion	100/100	100/100	100/100
Electro zinc-alloy plated steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	3.0	3.0	2.9
	Brine spraying (mm)	2.0	2.0	2.0
	Adhesion	100/100	100/100	100/100
Cold rolled steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.2	2.2	2.0
	Brine spraying (mm)	1.0	1.0	1.0
	Adhesion	100/100	100/100	100/100
	Spot rust (mm)	0.97	0.96	0.98

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Examples 9 to 13 and Comparative Example 9

The procedure of Examples 1 to 8 was repeated except that the surface conditioning step (FIXODINE 5N-5 treatment) was omitted. The composition of each

5 acidic aqueous phosphate solution is given in Table 3, and the spray treatment was effected at a spray pressure of 0.8 kg/cm^2 G and at a temperature of 52°C for 120 seconds. The data obtained with the resulting

10 phosphated plates, electrocoated plates, and coated plates with 3 coatings and 3 bakings, respectively, are given in Table 4.

Table 3

Composition of acidic aqueous phosphate solution	Example 9	Example 10	Example 11	Example 12	Example 13	Comparative Example 9
Zn ion (g/l)	1.0	1.0	1.0	0.7	1.2	0.7
PO ₄ ion (g/l)	14.0	14.0	14.0	14.0	20.0	14.0
Mn ion (g/l)	0.8	0.8	0.8	0.8	0.8	-
NI ion (g/l)	-	0.3	0.3	0.3	0.3	0.3
SiF ₆ ion (g/l)(as F ion)	1.0	1.0	2.0	1.0	1.0	-
NO ₂ ion (g/l)	0.06	0.06	0.06	0.06	0.06	0.06
H ₂ O ₂ (g/l)	-	-	-	-	-	-
NO ₃ ion (g/l)	4.0	4.0	4.0	4.0	4.0	4.0
ClO ₃ ion (g/l)	0.7	0.7	-	0.7	2.5	2.5
Total acidity (Point)	18.4	19.4	19.8	19.8	24.9	17.0
Free acidity (Point)	0.7	0.7	0.7	0.7	0.9	0.7
Acid ratio	26	28	28	28	28	24

Table 4

Metal	Test items	Example 9	Example 10	Example 11	Example 12	Example 13	Comparative Example 9
Galva-nealed steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.5	2.3	2.2	2.0	2.6	4.0
	Brine spraying (mm)	2.2	1.2	1.2	1.2	2.0	4.0
Electro-galvanized steel plate	Adhesion	100/100	100/100	100/100	100/100	100/100	95/100
	Adhesion	100/100	100/100	100/100	100/100	100/100	60/100
	Adhesion	100/100	100/100	100/100	100/100	100/100	100/100
Electro-zinc-alloy plated steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.0	2.0	1.8	1.8	2.0	4.0
	Brine spraying (mm)	3.2	2.0	1.2	2.2	2.7	7.0
Electro-zinc-alloy plated steel plate	Adhesion	100/100	100/100	100/100	100/100	100/100	0/100
	Adhesion	100/100	100/100	100/100	100/100	100/100	0/100
	Adhesion	100/100	100/100	100/100	100/100	100/100	0/100
Electro-zinc-alloy plated steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	2.8	2.5	2.2	2.4	2.5	3.5
	Brine spraying (mm)	2.0	1.7	1.0	1.7	1.7	3.5
Electro-zinc-alloy plated steel plate	Adhesion	100/100	100/100	100/100	100/100	100/100	50/100
	Adhesion	100/100	100/100	100/100	100/100	100/100	0/100
	Adhesion	100/100	100/100	100/100	100/100	100/100	0/100

Table 4 (continued)

Metal	Test items	Example 9	Example 10	Example 11	Example 12	Example 13	Comparative Example 9
Cold rolled steel plate	Film appearance	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent	Even, dense, excellent
	Film weight (g/m^2)	1.3	1.2	1.1	1.0	1.5	1.4
	Brine spraying (mm)	1.2	1.0	$1.0 \geq$	$1.0 \geq$	1.0	1.0
	Adhesion 2mm 1mm	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100	100/100 100/100
	Spot rust (mm)	0.95	0.94	0.92	0.95	0.96	0.95

Example 14

Phosphate films obtained in the foregoing Example 5 (treatment at 52°C) and Example 11 were respectively subjected to analysis in accordance with the previously given procedures for determining manganese content in the phosphate film. The results obtained are given in Table 5 below.

Table 5

Metal	Example 5 (treatment at 52°C)	Example 11
Galvanealed steel plate	Zn 34.5 wt. % Fe 0 " Mn 4.5 "	Zn 32.0 wt. % Fe 0 " Mn 4.5 "
Cold rolled steel plate	Zn 30.8 wt. % Fe 7.5 " Mn 5.1 "	Zn 28.8 wt. % Fe 5.7 " Mn 7.3 "

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CLAIMS

1. An acidic aqueous phosphate solution for phosphating a metal surface characterized in that the solution contains:
- a) from 0.1 to 2 g/l of zinc ion,
 - 5 b) from 5 to 50 g/l of phosphate ion,
 - c) from 0.2 to 4 g/l of manganese ion,
 - d) at least 0.05 g/l of a fluoride ion, and
 - e) a phosphating accelerator.
2. A solution according to claim 1 characterized by
- 10 containing at least one of the following quantities of ingredients:
- a) from 0.5 to 1.5 g/l of zinc ion,
 - b) from 10 to 30 g/l of phosphate ion,
 - c) from 0.6 to 3 g/l of manganese ion and
 - 15 d) from 0.1 to 3 g/l of a fluoride ion.
3. A solution according to claim 1 for the dip treatment of the metal surface characterized in that the solution contains:
- a) from 0.5 to 1.5 g/l of zinc ion,
 - 20 b) from 5 to 30 g/l of phosphate ion,
 - c) from 0.6 to 3 g/l of manganese ion,
 - d) at least 0.05 g/l of fluoride ion, and
 - e) a phosphating accelerator
4. A solution according to claim 3 characterized by
- 25 containing at least one of the following quantities of ingredients:
- a) from 0.7 to 1.2 g/l of zinc ion,
 - b) from 10 to 20 g/l of phosphate ion,
 - c) from 0.8 to 2 g/l of manganese ion, and
 - 30 d) from 0.1 to 2 g/l of a fluoride ion.

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5. A solution according to any one of the preceding claims characterized in that the fluoride ion in d) is a complex fluoride ion.

6. A solution according to claim 5 characterized in that the complex fluoride ion is the fluoroborate ion or the fluorosilicate ion.

7. A solution according to any one of the preceding claims characterized in that the phosphating accelerator in e) is at least one of the following:

- 10 i) chlorate ion,
- ii) nitrite ion,
- iii) nitrate ion,
- iv) hydrogen peroxide,
- v) m-nitrobenzene sulphonate ion,
- 15 vi) m-nitrobenzoate ion, and
- vii) p-nitrophenol.

8. A solution according to claim 7 characterized in that the phosphating accelerator is at least one of the following:

- 20 i) from 0.05 to 3 g/l of chlorate ion,
- ii) from 0.01 to 0.2 g/l of nitrite ion,
- iii) from 1 to 10 g/l of nitrate ion,
- iv) from 0.5 to 5 g/l of hydrogen peroxide
(based on 100% H_2O_2)
- 25 v) from 0.05 to 2 g/l of m-nitrobenzene
sulphonate ion,
- vi) from 0.05 to 2 g/l of m-nitrobenzoate ion,
and
- vii) from 0.05 to 2 g/l of p-nitrophenol.

20 9. A solution according to claim 8, characterized in that the phosphating accelerator is from 2 to 5 g/l of chlorate ion and the solution contains from >1 g/l to 2 g/l of zinc ion.

10. A solution according to any one of the preceding
25 claims characterized in that it also contains from 0.1 to 4 g/l of nickel ion.

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11. A solution according to claim 10 characterized in that the weight ratio of zinc ion to the sum of manganese ion and nickel ion is 1 : (0.5 to 5).
12. A solution according to claim 11 characterized in that the weight ratio of zinc ion to the sum of manganese ion and nickel is 1 : (0.8 to 2.5).
13. A solution according to any one of the preceding claims characterized in that the weight ratio of zinc ion to phosphate ion is 1 : (10 to 30).
- 10 14. A solution according to any one of the preceding claims characterized in that the weight ratio of zinc ion to manganese ion is 1 : (0.5 to 2).
15. A solution according to any one of the preceding claims characterized in that it has a total acidity of from 10 to 50 points, a free acidity of from 0.3 to 2.0 points and an acid ratio of from 10 to 50.
16. A process for phosphating a metal surface by treating the metal surface with an acidic aqueous phosphate solution characterized by employing as the solution a solution claimed in any one of the preceding claims.
17. A process according to claim 16 characterized by dipping the metal surface into the solution.
- 25 18. A process according to claim 17 characterized by dipping the metal surface into the solution for at least 15 seconds, followed by spraying the metal surface with the solution for at least 2 seconds.
19. A process according to claim 16 characterized by spraying the metal surface with the solution.
- 30 20. A process according to claim 19 characterized by spraying the metal surface with the solution for at least 5 seconds, followed by dipping the metal surface into the solution for at least 15 seconds.

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21. A process according to claim 19 characterized by using at least one cycle consisting of spraying the metal surface from from 5 to 30 seconds, discontinuing spraying for from 5 to 30 seconds, and then spraying 5 the metal surface for at least 5 seconds, the total spray time being at least 40 seconds.
22. A process according to any one of claims 17, 18 and 20 characterized in that the solution into which the metal surface is dipped is a solution 10 claimed in claim 3 or 4 or in any one of claims 5-15 when dependent directly or indirectly on claim 3 or 4.
23. A process according to any one of claims 16-22 characterized in that the treatment is carried out at a temperature of from 30 to 70°C.
- 15 24. A process according to any one of claims 16-23 characterized in that the metal treated includes both an iron-based surface and a zinc-based surface.
25. A process according to any one of claims 16-24 characterized in that the phosphated metal surface is 20 rinsed and electrocoated.
26. An aqueous concentrated composition for use in formulating an acidic aqueous phosphate solution characterized in that the concentrated composition comprises zinc ion, phosphate ion, manganese ion and 25 fluoride ion in a weight proportion of 0.1 to 2 : 5 to 50 : 0.2 to 4 : not less than 0.05.

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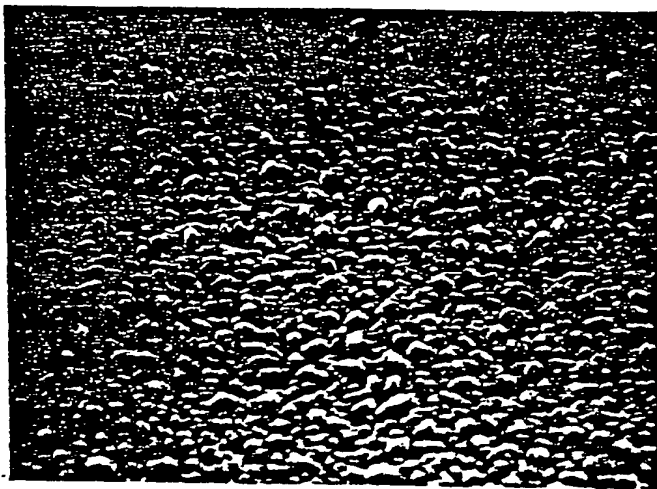


Fig-1

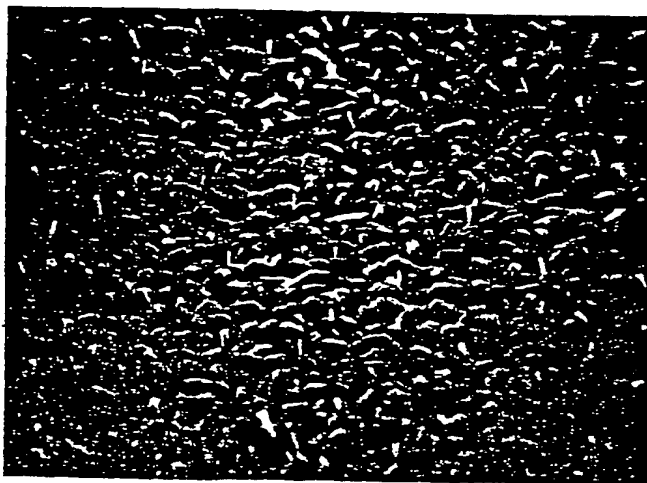


Fig-2

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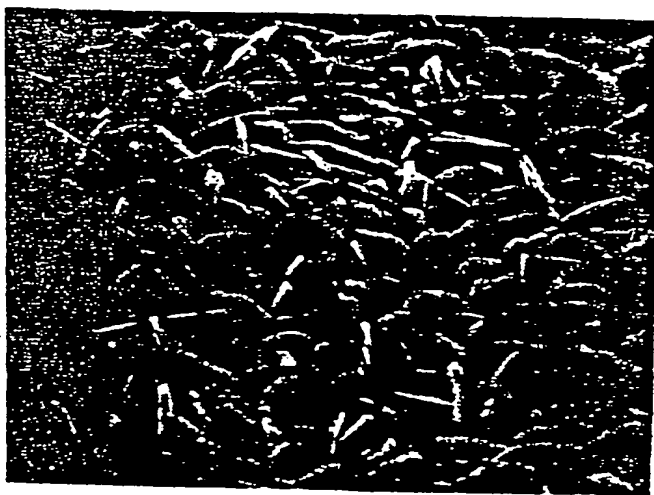


Fig-3

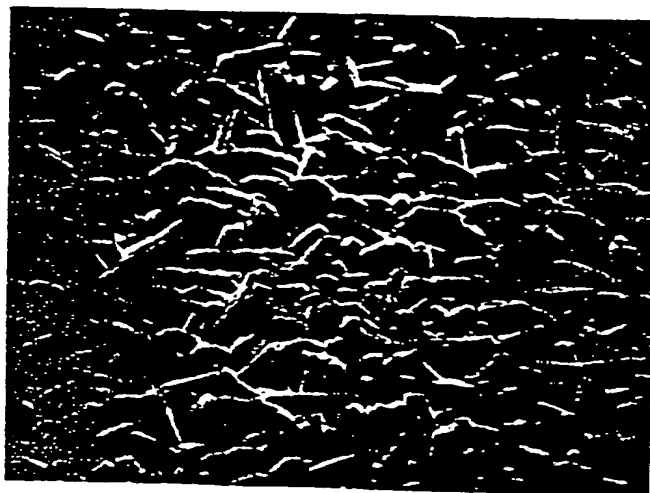


Fig-4



European Patent
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EUROPEAN SEARCH REPORT

0106459

Application number

EP 83 30 4885

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
D, X Y	EP-A-0 018 841 (NIPPON PAINT) * claims 1-3, 8, 14, 17; claims 18-20, 22-31; page 11, lines 2-5 *	1-8, 16	C 23 F 7/08
X, Y	EP-A-0 056 881 (METALLGESELLSCHAFT A.G.) * claims; page 7, lines 1-33; page 2, line 34 to page 3, line 12 *	1-14, 16, 17 19, 20 22-25	
D, Y	FR-A-2 449 135 (NIPPON PAINT) * claims; page 1, lines 14-33 *	1, 17, 18	
A	EP-A-0 042 631 (METALLGESELLSCHAFT A.G.)		TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
A	EP-A-0 036 689 (METALLGESELLSCHAFT A.G.)		C 23 F 7/08
A	FR-A-2 389 683 (SOC. CONT. PARKER)		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-12-1983	Examiner TORFS F.M.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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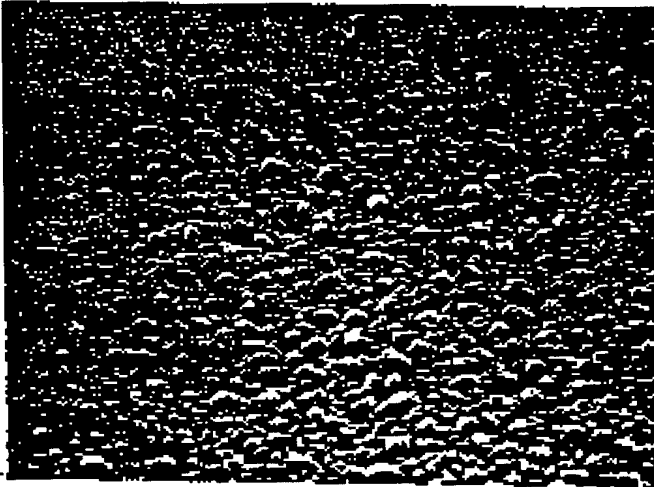


Fig-1

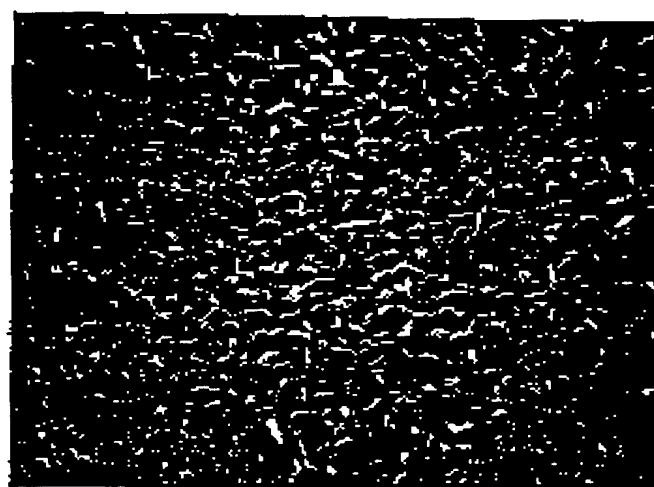


Fig-2

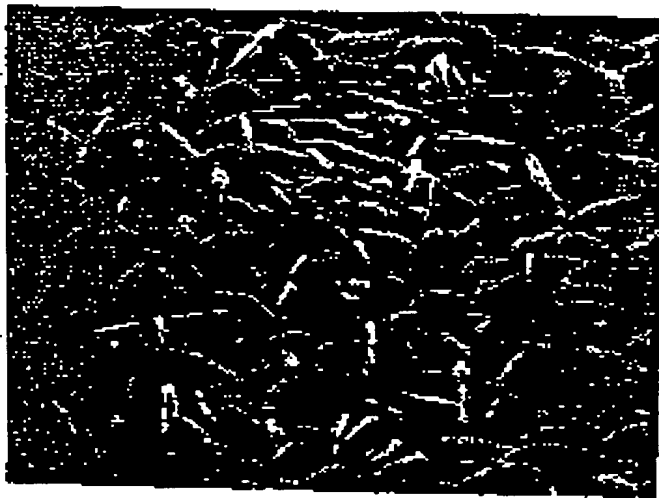


Fig. 3

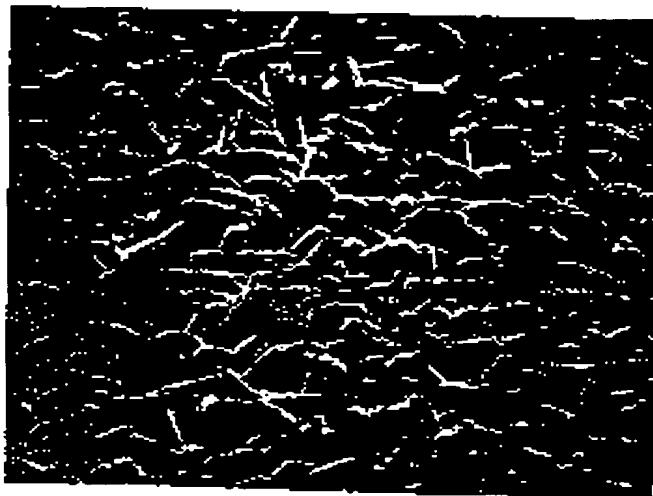


Fig. 4